Zeolite-promoted hydrolysis of cellulose in ionic liquid, insight into the mutual behavior of zeolite, cellulose and ionic liquid

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ABSTRACT

In this paper, a variety of H-type zeolites were demonstrated as efficient catalysts for hydrolysis of cellulose in ionic liquid (IL) to afford high yield of glucose under mild condition without a pretreatment process. By supplying water gradually as the reaction progresses, HY with the acid amount of 11.1 mol% promoted the highest glucose yield of 50.0% at 130 °C, and the yield of the three main products (glucose, cellobiose and 5-hydroxymethylfurfural) was up to 97.2%. It was found that the pore size, the acid amount, the water amount and the timing of water addition are critical factors for high hydrolysis efficiency. XRD characterization suggested that the framework structure of zeolite was particularly stable in 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), while the cell parameter were enlarged due to the dilatation effect of [BMIm]Cl. Elemental analysis of the IL-treated HY demonstrated that IL entered the channel of HY. As such, part of the intra-channel space of HY was occupied, making the average pore diameter, pore volume and the BET surface area of IL-treated HY all decreased, which were demonstrated by physisorption characterization. FT-IR through pyridine adsorption showed that H^+ cations generated in-situ from the Brönsted acid sites of zeolite were the key active species for the good hydrolysis performance, while the Lewis acid sites did not exhibit high activity. By simple calcination, the recovered HY showed excellent reusability. Finally, the proposed reaction pathway and recycle of the catalyst were presented.

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1. Introduction

Studies on the conversion of cellulose into biofuels and chemicals have been one of the most intensive pursuits worldwide [1–4]. Among various cellulose conversion processes, hydrolysis of cellulose to glucose is virtually an essential step in most practical cellulosic chemical or biofuel production [5]. However, cellulose is a highly crystalline polymer of D-anhydroglucopyranose unites jointed together in long chains by β-1,4-glycosidic bonds, the tight hydrogen-bonding network and van der Waals interactions greatly stabilize cellulose, making it indiscerptible in most solvents and thus notoriously resistant to hydrolysis [6,7].

Pioneer studies by Rogers and co-workers [8] showed that imidazolium-based ionic liquids (ILs) are a kind of powerful solvents that could dissolve cellulose. It thus opens an avenue for the conversion of cellulose in a homogeneous circumstance since it leaves the cellulose chains more accessible to chemical

transformations. Enlightened by this discovery, we firstly reported the hydrolysis behavior of cellulose in ionic liquids in the presence of mineral acids [9,10]. It was interesting to find that catalytic amounts of acid were sufficient to drive the hydrolysis reaction, while the traditional acid hydrolysis of cellulose in water was inefficient and cost-intensive. Through progressive addition of water during the course of cellulose hydrolysis, Raines [11] and Bell and Dee [12] further enhanced the hydrolysis efficiency. As the recovery of mineral acids is often difficult, we [13] and other groups [14–21] recently developed solid acids catalyzed hydrolysis of cellulose in water. However, because both cellulose and solid acids are typically not soluble in water, solid acids are generally much less effective than liquid acids. To achieve a high conversion of cellulose, the amount of solid acid used is commonly equal to [14,15], and even greater [13,15–20] than the amount of cellulose. Moreover, this process usually proceeds under harsh hydrothermal conditions with ball-milling pretreated cellulose [13,16,20]. To avoid the disadvantages and improve the efficiency, Schüth and co-workers [22,23] first reported the hydrolysis of cellulose over acid resin Amberlyst 15DRY in ionic liquid. In their catalytic system, cellulose undergoes selective depolymerization to yield exclusively cellulose oligomers (cellooligomers). In despite of these progresses, the above work focuses on the production of cellooligomers, and

more efficient process that favors β-1,4-glycosidic bonds cracking to afford high yield of glucose is to be developed. Furthermore, due to the unique ionic environment of ILs, the behavior of solid acid in ILs might be different from that exhibited in water, and the mutual interactions of solid acid, cellulose, as well as ionic liquids remain unclear yet.

In this paper, we focus on performing the depolymerization of cellulose over zeolites, a kind of solid acids containing both Lewis and Brönsted acid sites, in a controlled manner to afford high glucose yield in IL. By using XRD, physisorption, FT-IR, NH$_3$-TPD characterizations and element analysis, we provide new insights into the behavior of zeolite for cellulose hydrolysis in IL. A hydrolysis mechanism over zeolite in IL is proposed based on the catalytic results and the characterization. A catalyst recycle strategy is presented as well.

2. Experimental

2.1. Materials

Microcrystalline cellulose (extra pure, average particle size 90 μm) is purchased from Acros organics. HY (Si/Al = 4), HBeta (Si/Al = 25), HZSM-5 (Si/Al = 140) and SAPO-34 (Si/P/Al = 0.4/1/1) zeolites are purchased from Nankai University, China. [BMIm]Cl was prepared according to our previous study [9], the water content was determined as (0.0975 ± 0.0005)% through Karl–Fischer titration. All other chemicals were supplied by local suppliers and used without further purification.

2.2. Characterization methods

Elemental analysis of ionic liquid treated zelolite was done on a Vario MICRO elemental analyzer. X-ray diffraction (XRD) patterns of the catalysts were recorded on a PW3040/60 X'Pert PRO (PAN-alytical) diffractometer equipped with a Cu Kα radiation source (λ = 0.15432 nm), operating at 40 kV and 40 mA. The micropore-size distribution of the zeolites was measured by nitrogen adsorption at −196 °C on a Micromeritics ASAP 2010 instrument.

The acid densities of the zeolites were determined by NH$_3$-adsorption method, which was performed on a Micrometeritics Autochem 2910 instrument. Typically, 0.1 g of the zeolites was loaded into a quartz reactor and pretreated in Heat 200 °C for 2 h. After the sample was cooled to 100 °C in He stream, pulses of NH$_3$ were dosed in until saturation. The uptakes of NH$_3$ were auto-calculated accordingly.

The FT-IR spectra for pyridine adsorption were recorded on a Bruker spectrometer equipped with a MCT detector at a resolution of 4 cm^{-1}. Prior to pyridine adsorption, all samples were evacuated at 200 °C for 30 min, then cooled to room temperature. At this stage, the spectrum was collected as the background reference. Subsequently, pyridine was introduced for 5 min followed by evacuation for 30 min at room temperature. All the spectra were collected at room temperature and subtracted with the background reference.

2.3. Typical hydrolysis reaction process

All the experiments were carried out in a glass flask (10 ml). A typical reaction process is as follows: 0.1 g cellulose is dissolved in 2.0 g [BMIm]Cl at 130 °C, then 50.0 mg catalyst and 0.2 g H$_2$O were added into the mixture. The reaction samples were taken on schedule, weighed (M_1) and quenched with 1 ml cold water, weighed (M_2) and were centrifugated at a rate of 15,000 rpm for 10 min, then the upper clear liquid was pipetted off for HPLC analysis. The solid residue was direct transferred to pipe furnace for calcination in air (550 °C, 5 h) before used in the subsequent runs. The HPLC analysis of the products was conducted on Agilent 1100 with a Shodex

SC-101 column, using extra-pure water as mobile phase at a flow rate of 0.6 ml min^{-1}, the pressure of column was 24 bar, the column temperature was 75 °C. The yields of glucose, cellobiose and HMF were calculated by the equation: Yield (%) = (molar number of the product)/(molar number of gluco-units in cellulose) × 100%. Total yields were calculated by the equation: Total yield (%) = (Yield of glucose) + (Yield of cellobiose) × 2 + (Yield of HMF).

2.4. The treatment procedures of HY zeolite with ionic liquid [BMIm]Cl

0.2 g HY was added into 2.0 g [BMIm]Cl solvent and stirred at 130 °C for 9.5 h, and then, the reaction mixture was quenched with 10 ml cold water, and was subsequently centrifuged at the rate of 10,000 rpm for 10 min, the precipitation was washed three times with water and dried at 120 °C overnight to obtain the IL-treated HY.

3. Results and discussion

3.1. Preliminary study on zeolites promoted cellulose hydrolysis in IL

Table 1 summarizes the catalytic performances of various H-type zeolites, namely HY, HBeta, HZSM-5 and SAPO-34, for cellulose hydrolysis reaction in IL 1-butyl-3-methylimidazolium chloride ([BMIm]Cl). As a reference reaction, cellulose hydrolysis in water using HY as a catalyst was first tested. It was found that owing to the insolubility of cellulose and solid acid, the solid–solid interaction of cellulose and the catalyst was routinely inefficient, only trace amounts of products were detected at 100 °C in 5.5 h (entry 1). In sharp comparison, if the reaction was performed in [BMIm]Cl under otherwise identified conditions, the same catalyst could promote cellulose depolymerization to afford celloboise, glucose and 5-hydroxymethylfurfural (HMF) with the yields of 15.6%, 21.5%, and 3.3%, respectively, and the total yield of the three depolymerization products was 56.0% (entry 2). The comparative experiment clearly demonstrated that HY exhibited significantly improved catalytic activity in [BMIm]Cl than that in water. If the reaction temperature was increased to 130 °C, the yield of glucose and the total yield of the three depolymerization products could further enhance to 41.8% and 79.9%, respectively, within shorter time of 1 h (entry 3). In the meantime, the yield of cellobiose decreased, while the yield of HMF increased clearly from 3.3% to 13.9%, indicating that the elevated reaction temperature not only enhanced the rate of depolymerization of cellulose but also appeared to facilitate the dehydration of glucose into HMF. Besides the above mentioned products, trace amount of other soluble products, such as fructose, formic acid and levulinic acid were found in the reaction mixture. Cellooligmers with DP < 5 were another type of possible soluble products according to the reaction extent [22]. For the solid residue, it is difficult to identify unreacted cellulose or the insoluble side-products (e.g. polymerization products, humins, etc.) from the solid zeolite, but insoluble humins should have generated since the color of the solid residue turned black after reaction. We presume cautiously that in the initial stage of 1 h, there would contain unreacted cellulose in the mixture; thereafter, cellulose might be converted completely and insoluble side-products might form. This speculation was based on the following two facts: (1) 1 h is the time to get the highest depolymerization products yields (see in ESI, Fig. S2). (2) In our previous study using mineral acid as the catalyst for cellulose hydrolysis in IL [9], we found that given a proper reaction time, the reaction mixture could dissolve in water completely. Considering that unreacted cellulose could be precipitated in water, this fact suggests the complete conversion of cellulose at that time.

Table 1
The results of various zeolites catalyzed cellulose hydrolysis in [BMIm]Cl.[a]

Entry	Catalyst	Acid density (mmol g^{-1})[b]	Acid amount (mol%)[c]	Dp (nm)[d]	Time (h)	Yield (%)			
						Cellobiose	Glucose	HMF	Total
1	HY[e,f]	1.36	11.1	0.74 × 0.74	5.5	Trace	Trace	0	Trace
2	HY[f]	1.36	11.1	0.74 × 0.74	5.5	15.6	21.5	3.3	56.0
3	HY	1.36	11.1	0.74 × 0.74	1	13.4	41.8	11.2	79.9
4	HY	1.36	6.6	0.74 × 0.74	0.5	13.8	15.9	1.5	45
5	HY	1.36	11.1	0.74 × 0.74	0.5	17.8	27.8	4.8	68.2
6	HY	1.36	17.7	0.74 × 0.74	0.5	12.5	41.2	12.7	78.9
7	HBeta	0.88	11.1	0.66 × 0.67 0.56 × 0.56	1	18.1	33.3	4.8	74.3
8	HZSM-5	0.51	11.1	0.53 × 0.56 0.51 × 0.55	1	15.1	18.1	1.5	49.9
9	SAPO-34	0.15	11.1	0.38 × 0.38	1	1.1	0.6	0	2.9
10	HBeta	0.88	11.1	0.66 × 0.67 0.56 × 0.56	2	13.5	41.5	8.6	77.0
11	HZSM-5	0.51	11.1	0.53 × 0.56 0.51 × 0.55	3.5	15.2	42.3	8.2	80.9
12	HY[g]	1.36	11.1	0.74 × 0.74	5.5	26.2	34.4	10.5	97.2
13	HY[h]	1.36	11.1	0.74 × 0.74	2	5.3	50.0	23.6	84.3
14	HY-IL[i]	0.39	3.2	0.54 × 0.54	2.5	9.2	12.4	1.4	23.1

[a] Unless otherwise specified, the reactions were conducted in 2.0 g [BMIm]Cl at 130 °C with 0.1 g microcrystal cellulose, in the presence of 0.2 g H_2O and appropriate amount of catalyst.

[b] The acid density was determined by an NH_3-adsorption method.

[c] Acid amount = (acid density × mass of catalyst)/(molar of gluco-units in cellulose) × 100%.

[d] The pore dimensions of the catalysts were obtained from the supplier.

[e] 2.0 g water was employed as the reaction medium.

[f] The reaction temperature was 100 °C.

[g] The reaction was performed by adding water gradually: 5% (0 min), 20% (10 min), 25% (20 min), 33% (30 min) and 43% (60 min), water content is relative to the total mass of the reaction mixture and is shown at time points (minutes) following the initiation of hydrolysis.

[h] The reaction process is similar to entry 12, except that the water amount and the timing of water addition are: 5% (0 min), 20% (30 min), 33% (60 min).

[i] The catalyst was treated in [BMIm]Cl for 9.5 h, and then washed with water extensively and dried before use.

For cellulose hydrolysis reaction, one of the key issues that affect the results is the acidity. In IL system, it was found that the higher the amount of solid acid, the faster the hydrolysis reaction rate. For instance, starting with 6.6 mol% HY at 130 °C for 0.5 h, the hydrolysis reaction only afforded glucose yield and the total yield of the main depolymerization products 15.9% and 45%, respectively (Table 1, entry 4); the reaction with increased amount of HY (11.1 mol% and 17.7 mol%) could afford enhanced results of glucose 27.8% and 41.2%, total products 68.2% and 78.9%, respectively (entries 5–6). On the other hand, it is interesting to note that all the reactions could achieve similar highest glucose yields of ca. 40%, with the total yields of the main depolymerization products ca. 80%, despite that the acid amount are various (ESI, Fig. S1–3). The above results implied that the acid amount only affects the hydrolysis rate, whereas it will not change the maximum yield under the relatively mild condition applied herein.

For most of the zeolites catalyzed chemical reactions, the pore size of zeolite should be an important factor that affects the catalytic activity. To clarify the influence of the pore size on hydrolysis efficiency, four kinds of zeolites containing the same amount of acid and different pore sizes were employed in cellulose hydrolysis reaction. It was found that the catalytic performance of the catalyst increased with the increasing of the pore size. For example, HY with the largest pore diameter (0.74 nm × 0.74 nm) promoted the highest yields of depolymerization products in 1 h (Table 1, entry 3). HBeta and HZSM-5 with middle pore sizes of 0.66 × 0.67/0.56 × 0.56 nm and 0.53 × 0.56/0.51 × 0.55 nm (entries 7–8) exhibited moderate glucose yields of 33.3%, 18.1% and total yields of 74.3% and 49.9%, respectively. For zeolite SAPO-34, it contains the smallest pore diameter of 0.38 nm × 0.38 nm, accordingly, the hydrolysis efficiency is the poorest (entry 9). Therefore, zeolite with large pore size favors cellulose hydrolysis. This phenomenon seems similar to that demonstrated in water solvent [24]; however, they are basically different in the way that affects the catalytic activity. In water solvent, zeolite catalyzed cellulose hydrolysis is a typical heterogeneous reaction, and small pore size could restrain the entering of cellulose, a large polymer molecule of gluco-units, in zeolite pores and thus decrease the contact probability between cellulose and the acid sites. Whereas in IL system, the hydrolysis performance is in fact not related to cellulose moving into the pores, but the cation of the IL, which can react with the Brönsted acid sites of HY via ion exchange to release H^+ (This viewpoint will be proved in detail later in Section 3.2). Indeed, we have tried to correlate the ion exchange rate, or the proton release rate, with the performance of the catalysts. After zeolite was stirred in [BMIm]Cl at 130 °C for 1 h, it was found that the released proton of the four zeolites were 25.3 μmol, 22.5 μmol, 17.5 μmol and 5.6 μmol, respectively for HY, HBeta, HZSM-5 and SAPO-34 [25]. Obviously, the larger the pore size of zeolite, the faster the proton release rate, and the higher the performance of the hydrolysis reaction (Table 1, entries 3, 7–9). Interestingly, given enough reaction time, HBeta and HZSM-5 with middle pore sizes could also give rise to high yields of glucose over 40%, with the yields of the three main depolymerisation products ca. 80% (entries 10–11), which were similar to that obtained with HY (entry 3).

It is known that in cellulose hydrolysis reaction system, water acts as a substrate; on the other hand, excessive water can precipitate cellulose from ionic liquid, making homogeneous hydrolysis of cellulose in ionic liquid impossible; moreover, as water is a product in glucose dehydration reaction, abundant water in reaction system could stabilize glucose. Therefore, water should play a complex but critical role in cellulose hydrolysis reaction. To identify the influence of water, we attempted to balance cellulose solubility and glucose stability by adding water gradually as the reaction progresses, expecting that cellulose hydrolysis efficiency would further increase. As can be seen from Table 1, entry 12, when the reaction mixture was gradually diluted to 43% water content within the first 1 h, the reaction proceeded very slow, resulting in 34.4% glucose yield, and 26.2% of incomplete hydrolysis product cellobiose. However, the total yield of the three main products
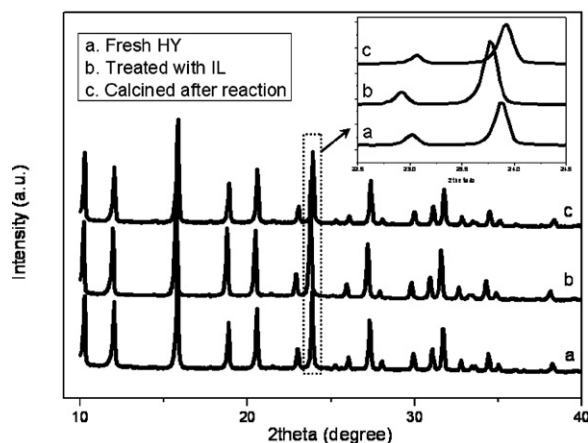
Fig. 1. XRD patterns of HY zeolite before and after reaction. (a) Fresh HY; (b) after reaction, HY was collected, washed with water and dried at 120 °C for 12 h before characterization; (c) sample (b) was calcined at 550 °C for 5 h before characterization.

Fig. 2. Pore size distribution calculated by using the HK method with the N_2 desorption isotherm. Samples were the same as those used in Fig. 1.

were up to 97.2%, which was much higher than that obtained in the reaction mixture with 10 wt% water (entry 3 vs 12). Apparently, the side reactions for humins and other degradation products are remarkably restrained in water abundant system. Noting that cellobiose concentrations peaked at 30 min in 10% water mixture (see in ESI, Fig. S2), additional water was supplied after 30 min to allow cellobiose hydrolyze complete to glucose. In this case, improved glucose yield of 50.0%, with the total yield of 84.3% were obtained in 2 h. Therefore, water amount and the timing of water addition are two critical factors for high hydrolysis efficiency. These results were in accordance with what has been reported using mineral acid as catalyst for cellulose hydrolysis in ILs [11,12].

As described earlier, to achieve a better performance, most of the reactions catalyzed by solid acids are usually conducted under harsh hydrothermal conditions with large amount of solid acids. One of the major advantages of the present study is that the acid densities of the applied zeolites are in the range of 0.15–1.36 mmol g^{-1}, which accounted for only 6.6–17.7 mol% of gluco-units in cellulose (Table 1). Furthermore, our reactions were performed at a relatively lower temperature (130 °C) and under atmosphere pressure. Apparently, the present hydrolysis proceeded at a mild condition with reduced acid loading and without compromising the glucose yield (in solid acids catalyzed cellulose hydrolysis, the glucose yields are commonly lower than 50%, the exceptional example over 50% was obtained in our lab by using excessive amount of sulfonated carbon as catalyst reacting at 150 °C for 24 h [13]).

3.2. Characterization of the zeolite behavior in ionic liquid

It is known that zeolites are a kind of solid acids containing both Lewis and Brönsted acid sites. To explore the nature of zeolite-promoted cellulose hydrolysis in ionic liquids, and to provide direct insight into the mutual interactions of zeolite, cellulose, as well as IL during the hydrolysis process, taking HY as an example, a series of physical and chemical characterizations were conducted.

Fig. 1 shows the XRD patterns of fresh HY (a), the IL-treated HY (b) and the recovered HY after calcination (c). It can be seen that the intensity and the numbers of diffraction peaks of samples (b) and (c) were the same as those of the fresh one. It thus suggested that the framework structure of HY was particularly stable in [BMIm]Cl. On the other hand, it was intriguing to find that the peaks of sample (b), IL-treated HY, were entirely moved a little (ca.
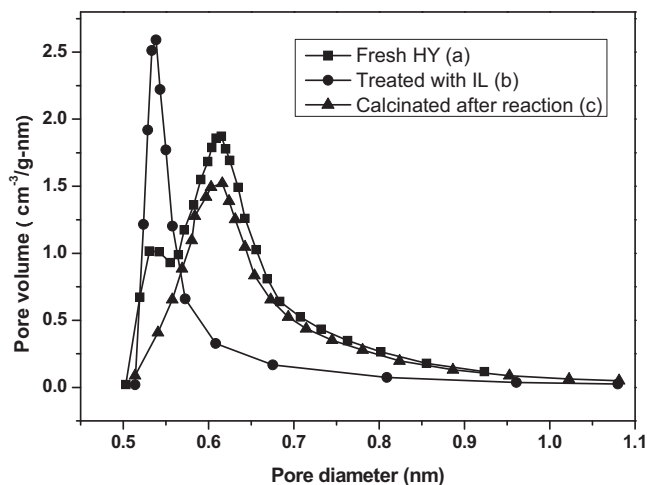
0.111°) to lower angle values than those of fresh catalyst. According to Bragg equation [26], the slight shift in peak's position implied that the interplanar spacing d-spacing increased after reaction. Further calculation through MDIJade5.0 software showed that for a cubic lattice, the cell parameters of the three samples of (a), (b), and (c), were 24.41 Å, 24.49 Å, and 24.46 Å, respectively. Apparently, the cell parameter of HY was enlarged after treatment with IL. The increase in the cell parameter was probably due to the dilatation effect of [BMIm]Cl that entered the pore of HY, which will be further discussed later in combination with physisorption, FT-IR characterizations and element analysis.

To further explore the change in structure, the pore size distribution profiles of the zeolite samples were characterized. It was found in Fig. 2 that the average pore diameter, the average pore volume and the BET surface area of the fresh HY were detected as 0.62 nm, 0.29 cm^3/g and 671.46 m^2/g, respectively, using N_2 as an adsorbate. However, the corresponding values of IL-treated HY were decreased to 0.55 nm, 0.14 cm^3/g and 307.29 m^2/g, respectively. The above comparative results are in according with our hypothesis that IL might have entered and occupied some of the intra-channel space in HY. Elemental analysis of IL-treated HY confirmed this hypothesis. It is known that HY zeolite consists of H, O, Si and Al elements. However, elemental analysis of the IL-treated HY revealed that besides the above elements, N and C mass contents of 2.25% and 8.14% with the N/C molar ratio of 1:4 were detected, which was matching with the N/C molar ratio in 1-butyl-3-methylimidazolium cation ([BMIm]$^+$), whose molecule formula is [C$_8$H$_{15}$N$_2$]$^+$. Evidently, by simple mixing HY with IL, [BMIm]Cl has entered the inner channel of HY and has been anchored in HY via chemical interaction, regarding that [BMIm]Cl readily dissolves in water, and sample (b) has been extensively washed with water and dried before characterization. It is found that after calcination, the average pore diameter, pore volume and the BET surface area of IL-treated HY were detected as 0.62 nm, 0.25 cm^3/g and 628.09 m^2/g, respectively, which were similar to those of the fresh one. The results indicated that IL that entered the inner channel of HY could be removed and the structure of HY could be recovered by simple calcination. It should be noted that according to Maier's [27] study, the pore sizes in the micropore range obtained with nitrogen as the adsorbate are usually lower than the real ones. For instance, the pore size of NaY was detected as 0.63 nm and 0.74 nm with nitrogen and argon, respectively [27]. Since the detected datum was 0.62 nm in our study with nitrogen as the adsorbate, the real average pore diameter of the fresh HY was estimated as ca. 0.74 nm.
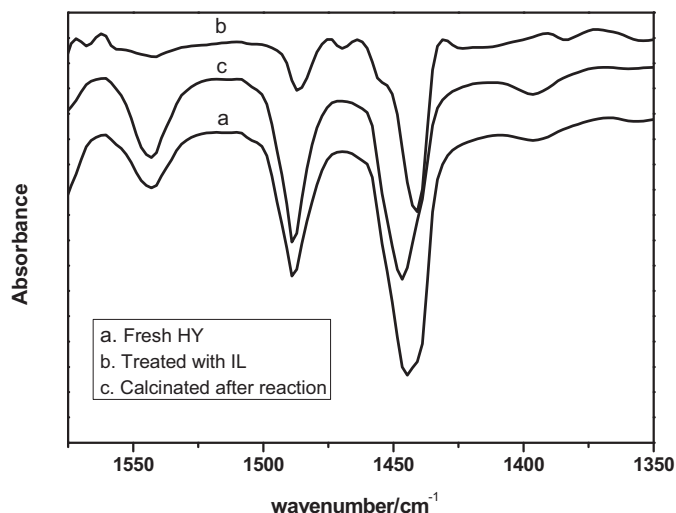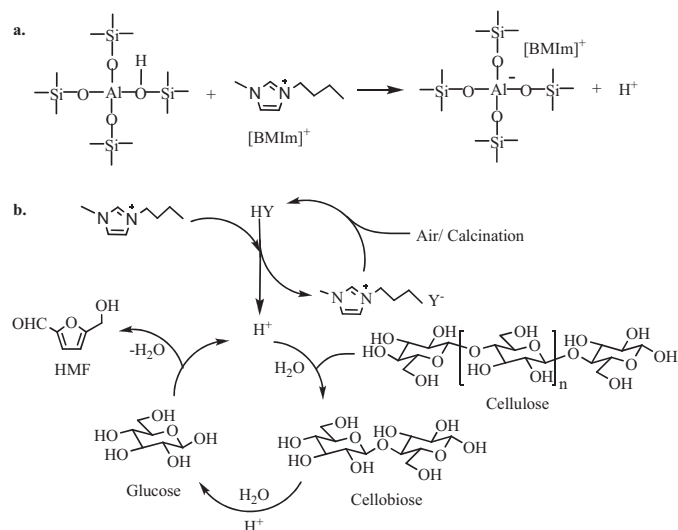
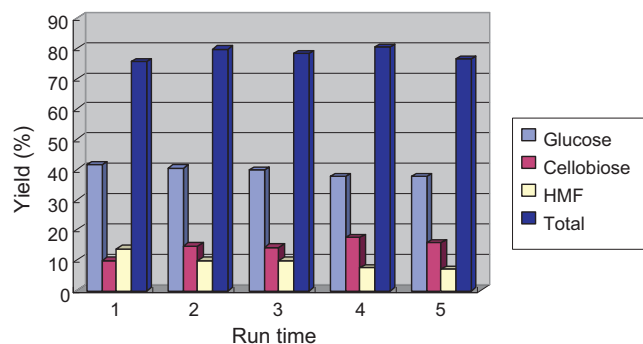**Fig. 3.** FTIR pyridine adsorption of HY zeolite. Samples were the same as those used in Fig. 1.

Fig. 4. The recycle results of HY catalyzed cellulose hydrolysis in [BMIm]Cl. The reactions were conducted in 2.0 g [BMIm]Cl at 130 °C with 0.1 g microcrystal cellulose, in the presence of 0.2 g H_2O and 0.05 g of catalyst.

Regarding that HY contains both Lewis and Brönsted acid sites, to uncover the function of each acid sites, we investigated the acidity of HY with FT-IR through pyridine adsorption. As can be seen in Fig. 3, both Brönsted acid sites ($\sim$1545 cm^{-1}) and Lewis acid sites ($\sim$1448 cm^{-1}) existed in fresh HY zeolite (sample a). However, after treated with ILs for 9.5 h, nearly no Brönsted acid site was detected in IL-treated HY (sample b). In according with the elemental analysis results that [BMIm]$^+$ has entered the inner channel of HY and has been anchored in HY, the above fact implied that the Brönsted acid sites of HY, in the form of H$^+$, have released via ion-exchange with ILs, as illustrated in Scheme 1a. In contrast, the amount of Lewis acid sites ($\sim$1448 cm^{-1}) only slightly decreased after treated with IL (sample b), suggesting that the Lewis acid sites were more stable during the reaction process. With this catalyst for hydrolysis reaction only gave much poorer yields of depolymerization products (Table 1, entry 14) than those of fresh HY. The results suggested that although Lewis acid sites may work in cellulose hydrolysis reaction, the key active species that responsible for the good performance of HY should be Brönsted acid sites. Nevertheless, the stability of Lewis acid sites of HY in ILs provides us an opportunity for trying Lewis acid catalyzed other chemical transformations. It is important to

note that after calcination at 550 °C, the acid sites of the recovered HY were regenerated, and the strength of the peaks of both Lewis and Brönsted acids were nearly the same as those of the fresh one (sample c). Therefore, another advantage of the present study is that no additional acid was needed for the regeneration of the catalyst. In contrast, washing with strong mineral acid is commonly necessary for the regeneration of acid resin [22].

3.3. Recycling potential of the catalyst and mechanism consideration

Using the calcinated catalyst, we tested the reusability. One can see in Fig. 4 that the yields of glucose and the total depolymerization products were almost maintained for at least five runs. Therefore, by simple calcination, the acid sites of HY could be regenerated, and the recovered HY showed excellent reusability in our reaction system.

Based on the characterizations and the catalytic results above, we proposed the reaction pathway of HY catalyzed cellulose hydrolysis in IL (Scheme 1). Initially, HY zeolite in [BMIm]Cl solvent could make [BMIm]$^+$ enter the inner channel of HY. The IL then reacted with the Brönsted acid sites of HY to release H$^+$ (Scheme 1a), which can subsequently catalyze cellulose hydrolysis homogeneously to produce cellobiose and glucose. Part of glucose could then further dehydrate to form HMF under acid circumstance (Scheme 1b). After the reaction, the acid sites of the catalyst were regenerated through simple calcination, and the catalyst was used directly in the subsequent run. As such, the catalytic activity was well maintained. The high efficiency of zeolite/IL system is mainly due to the following three aspects. First, cellulose is completely dissolved in IL to form a homogeneous solution, it makes the catalyst more accessible to the β-glucosidic bonds [9,10]; second, the dissociated Cl$^-$ and the electron-rich aromatic π system of [BMIm]$^+$ in [BMIm]Cl could weaken the glycosidic linkage to facilitate hydrolysis [8]; additionally, the ion exchange of IL with HY promoted the generation of H$^+$ from Brönsted acid sites of HY, which could readily contact cellulose in IL.

4. Conclusions

In summary, the combination of a variety of zeolites with IL were demonstrated as efficient systems for hydrolysis of cellulose under mild condition without a pretreatment process. It was found that the pore size, the acid amount, the water amount and the timing of water addition are critical factors for high hydrolysis efficiency. By using XRD, physisorption, FT-IR, NH$_3$-TPD characterizations and element analysis, we provide new insights into the behavior of zeolite for cellulose hydrolysis in ionic liquid. A proposed hydrolysis mechanism over zeolite in ionic liquid is presented based on the

Scheme 1. Proposed reaction pathway and recycle of HY.

catalytic results and the characterization. One of the major advantages of the present study is that the acid loading is much less than the conventional solid acid catalyzed cellulose hydrolysis reaction. Another advantage is that the activity of recovered HY could be regenerated via simple calcination, therefore, no additional acid was needed for the regeneration of the catalyst.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2012.04.041.

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